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Publication number:

0 304 001  
A2

(12)

# EUROPEAN PATENT APPLICATION

(21) Application number: 88113218.7

(51) Int. Cl.<sup>4</sup> G03C 7/38 , //C07D231/54

(22) Date of filing: 16.08.88

(30) Priority: 18.08.87 JP 203450/87  
18.08.87 JP 203451/87

(43) Date of publication of application:  
22.02.89 Bulletin 89/08

(84) Designated Contracting States:  
DE GB IT NL

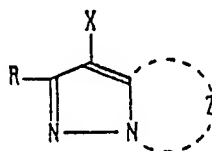
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(54) Coupler for photographic use.

(57) A novel cyan color-forming coupler for photographic use is disclosed. The coupler has a improved fastness for heat, humidity, and has a chemical structure represented by the following Formula I;  
Formula I



wherein Z is a group of non-metal atoms necessary for completing a nitrogen-containing six-member heterocyclic ring condensed with the pyrazole ring. The six-member ring may be substituted or not substituted provided that the six-member ring does not have be condensed with any ring other than the pyrazole ring; R represents a hydrogen atom or a substituent, and X represents a hydrogen atom or a substituent capable of being split off upon reaction with the oxidized product of a color developing agent.

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## COUPLER FOR PHOTOGRAPHIC USE

## FIELD OF THE INVENTION

5 This invention relates to a novel coupler for photographic use to serve as a color photographic material and particularly to a coupler for photographic use which is capable of forming a dye image excellent in fastness against temperature, moisture and light.

10 BACKGROUND OF THE INVENTION

When a silver halide photographic light-sensitive material is exposed to light and is then color-developed, a dye is produced in the light-exposed areas of the light-sensitive material upon reaction of an oxidized aromatic primary amine color developing agent with a dye-forming coupler, so that a color image is formed.

Generally, in this photographic method, a color subtractive reproduction process is used to form each of yellow, magenta and cyan images.

For example, the couplers for photographic use for forming the above-mentioned yellow color images include acylacetanilide type couplers; those for forming the magenta color images include pyrazolone type, pyrazolobenzimidazole type, pyrazolotriazole type or indazolone type couplers; and those for forming the cyan color images include phenol type or naphthol type couplers; each of which is generally used.

The dye images thus prepared have been so required as not to be discolored even if they are exposed to light for a long time or are stored at a high temperature and a high humidity.

25 The phenol type and naphthol type couplers have been studied so far to serve as the couplers for forming cyan dyes. However, they are as yet not quite satisfactory in the spectral absorption characteristics, resistance against heat, moisture and light, and so forth. Aiming at the improvements of these problems, there have been various proposals including those for devised substituents. But, no compound is not obtained yet to solve the above-mentioned problems.

30

## SUMMARY OF THE INVENTION

35 It is an object of the invention to provide a coupler for photographic use which can be used as a color photographic material.

Another object of the invention is to provide a coupler for photographic use which is capable of forming cyan dye images having a hue not changeable against heat, moisture and light.

The above-mentioned objects of the invention can be accomplished with a coupler for photographic use which is represented by the following formula I.

40 Formula I



50 wherein Z is a group of non-metal atoms necessary to complete a nitrogen-containing 6-membered heterocyclic ring upon condensation-cyclization with the pyrazole ring, provided that the 6-membered ring may have a substituent, but is not condensed with other rings than the pyrazole ring; R represents a hydrogen atom or a substituent; and X represents a hydrogen atom or a substituent capable of being split off upon reaction with the oxidized product of a color developing agent.

## DETAILED DESCRIPTION OF THE INVENTION

The couplers for photographic use, which relates to the invention, are so constituted as to form a 6-membered heterocyclic ring upon condensation with a pyrazole ring. There is no special limitation to the substituents represented by R, however, typical examples thereof include each group of alkyl, aryl, anilino, acylamino, sulfonamido, alkylthio, arylthio, alkenyl, cycloalkyl and so forth and, besides, a halogen atom, each group of cycloalkenyl, alkynyl, heterocyclic, sulfonyl, sulfinyl, phosphonyl, acyl, carbamoyl, sulfamoyl, cyano, alkoxy, sulfonyloxy, aryloxy, heterocyclic oxy, siloxy, acyloxy, carbamoyloxy, amino, alkylamino, imido, ureido, sulfamoylamino, alkoxy-carbonylamino, aryloxy-carbonylamino, alkoxy-carbonyl, aryloxy-carbonyl, heterocyclic thio, thioureido, carboxy, hydroxy, mercapto, nitro, sulfonic acid and so forth, a spiro compound residual group, a bridged hydrocarbon compound residual group, and so forth.

The alkyl groups represented by R may preferably be those having 1 to 32 carbon atoms and they may further be straight-chained or branched.

The aryl groups represented by R include, preferably, a phenyl group.

The acylamino groups represented by R include, for example, each group of alkylcarbonylamino, arylcarbonylamino and so forth.

The sulfonamido groups represented by R include, for example, each group of alkylsulfonylamino, arylsulfonylamino and so forth.

The alkyl and aryl components of the alkylthio and arylthio groups each represented by R include, for example, the alkyl and aryl groups each represented by the R.

The alkenyl groups represented by R include, for example, those having 2 to 32 carbon atoms; the cycloalkyl groups include, preferably, those having 3 to 12 carbon atoms and, more preferably, those having 5 to 7 carbon atoms, and the alkenyl groups may be straight-chained or branched.

The cycloalkenyl groups represented by R include, preferably, those having 3 to 12 carbon atoms and, more preferably, those having 5 to 7 carbon atoms.

The sulfonyl groups represented by R include, for example, each group of alkylsulfonyl, arylsulfonyl and so forth;

The sulfinyl groups include, for example, each group of alkylsulfinyl, arylsulfinyl and so forth;

The phosphonyl groups include, for example, each group of alkylphosphonyl, alkoxyphosphonyl, aryloxyphosphonyl, arylphosphonyl and so forth;

The acyl groups include, for example, each group of alkylcarbonyl, arylcarbonyl and so forth;

The carbamoyl groups include, for example, each group of alkylcarbamoyl, arylcarbamoyl and so forth;

The sulfamoyl groups include, for example, each group of alkylsulfamoyl, arylsulfamoyl and so forth,

The acyloxy groups include, for example, each group of alkylcarbonyloxy, arylcarbonyloxy and so forth;

The carbamoyloxy groups include, for example, each group of alkylcarbamoyloxy, arylcarbamoyloxy and so forth;

The ureido groups include, for example, each group of alkylureido, arylureido and so forth;

The sulfamoylamino groups include, for example, each group of alkylsulfamoylamino, arylsulfamoylamino and so forth;

The heterocyclic groups include, preferably, those having 5 to 7-membered ring and, typically, each group of 2-furyl, 2-thienyl, 2-pyrimidinyl, 2-benzothiazolyl, 1-pyrrolyl, 1-tetrazolyl and so forth;

The heterocyclic oxy groups include, preferably, those having a 5 to 7-membered heterocyclic ring and, typically, each group of 3,4,5,6-tetrahydropyran-2-yl, 1-phenyltetrazole-5-yl and so forth;

The heterocyclic thio groups include, preferably, those having 5 to 7-membered ring and, typically, each group of 2-pyridylthio, 2-benzothiazolylthio, 2,4-diphenoxy-1,3,5-triazole-6-thio, and so forth;

The siloxy groups include, for example, each group of trimethylsiloxy, triethylsiloxy, dimethylbutylsiloxy, and so forth;

The imido groups include, for example, each group of succinimido, 3-heptadecyl succinimido, phthalimido, glutarimido and so forth;

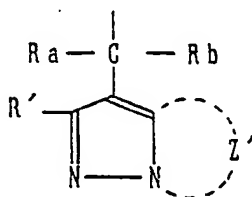
The spiro compound residual groups include, for example, each group of spiro [3.3] heptane-1-yl and so forth;

The bridged hydrocarbon compound residual groups include, for example, each group of bicyclo [2.2.1] heptane-1-yl, tricyclo [3.3.1.1<sup>37</sup>] decane-1-yl, 7,7-dimethyl-bicyclo [2.2.1] heptane-1-yl, and so forth.

The above-given groups are further allowed to have such a substituent as a ballast group including a long-chained hydrocarbon group, a polymer residual group and so forth.

X represents a group capable of being split off upon reaction with the oxidized product of a color developing agent. The groups include, for example, a halogen atom such as each atom of chlorine,

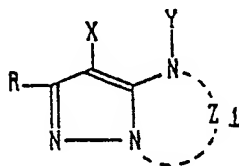
bromine, fluorine and so forth and each group of alkoxy, aryloxy, heterocyclic oxy, acyloxy, sulfonyloxy, alkoxy-carbonyloxy, aryloxy-carbonyl, alkoxy-oxalyloxy, alkoxy-oxalyloxy, alkylthio, arylthio, heterocyclic thio, alkoxythiocarbonylthio, acylamino, sulfonamido, nitrogen-containing heterocyclic ring bonded with an N atom, alkoxy-carbonylamino, aryloxy-carbonylamino, carboxyl, and



wherein R' is synonymous with the above-given R, Z' is synonymous with the above-given Z, and Ra and Rb each represent a hydrogen atom, an aryl group, an alkyl group or a heterocyclic group, and so forth; and, preferably, a halogen atom. Among these groups, the particularly preferable ones include a hydrogen atom and a chlorine atom.

The typically preferable examples of the compounds represented by Formula I are represented by the following formula II.

Formula II



wherein Z1 represents a group of non-metal atoms necessary to complete a nitrogen-containing 6-membered heterocyclic ring so as to contain at least one -NY- and at least one carbonyl group, upon condensation-cyclization with the pyrazole ring, provided that the 6-membered ring may have a substituent but may not be condensed with any other ring than the pyrazole ring; R and Y each represent a hydrogen atom or a substituent; and X represents a hydrogen atom or a substituent capable of being split off upon reaction with the oxidized product of a color developing agent.

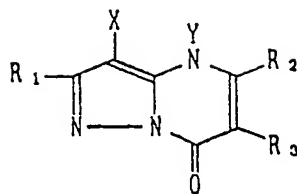
The compounds represented by Formula II will now be described further in detail.

In Formula II, the nitrogen-containing 6-membered heterocyclic ring formed by Z1 should preferably be those of either 6 $\pi$  or 8 $\pi$  electron system, which contains 1 to 4 nitrogen atoms including at least one -NY-. At least one carbonyl group contained in the 6-membered ring represents such a group as >C=O, >C=S and so forth; and R and X are synonymous with R and X denoted in Formula I, respectively.

In Formula II, Y represents a hydrogen atom or a substituent. The preferable substituents represented by Y are those capable of being split off from the above-mentioned compounds upon reaction of the compounds of the invention with the oxidized product of a color developing agent. The substituents represented by Y include those capable of being split off under an alkaline condition such as described in Japanese Patent Publication Open to Public Inspection (hereinafter referred to as Japanese Patent O.P.I. Publication) No. 228444-1986 and so forth, those capable of coupling off upon reaction with the oxidized product of a color developing agent such as described in Japanese Patent O.P.I. Publication No. 133734-1981 and so forth. However, the preferable one represented by Y should be a hydrogen atom.

Among the compounds represented by Formula II, the most preferable examples should be the compounds represented by the following formula III or IV.

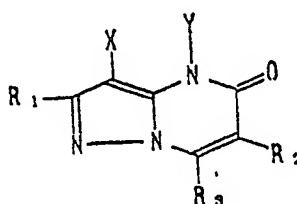
Formula III



10 wherein  $R_1$ ,  $R_2$  and  $R_3$  are synonymous with  $R$  denoted in Formula I;  $X$  is synonymous with  $X$  denoted in Formula I; and  $Y$  is synonymous with  $Y$  denoted in Formula II.

In Formula III,  $R_2$  and  $R_3$  are synonymous with  $R$  denoted in Formula I, however,  $R_2$  cannot be a hydroxy group.

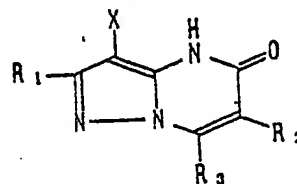
15  $R_2$  and  $R_3$  preferably represent, for example, each group of alkyl, aryl, carboxyl, oxycarbonyl, cyano, alkoxy, aryloxy, amino, amido, sulfonamido and so forth, each atom of hydrogen and halogen, and so forth.  
Formula IV



wherein  $R_1$ ,  $R_2$  and  $R_3$  each are synonymous with the  $R$  denoted in Formula I; and  $X$  and  $Y$  each are synonymous with  $X$  and  $Y$  denoted in Formula II, respectively; however, in the compounds represented by Formula IV, it is preferred that  $Y$  represents a hydrogen atom, that is to say, the compounds represented by

30 the following Formula V.

Formula V



wherein  $R_1$ ,  $R_2$ ,  $R_3$  and  $X$  each are synonymous with  $R_1$ ,  $R_2$ ,  $R_3$  and  $X$  denoted in the compounds represented by Formula IV.

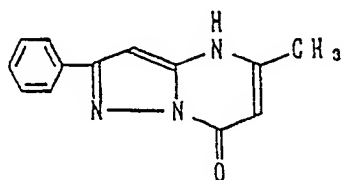
45 Next, the typical examples of the compounds of the invention will be given below. It is, however, to be understood that the invention shall not be limited thereto.

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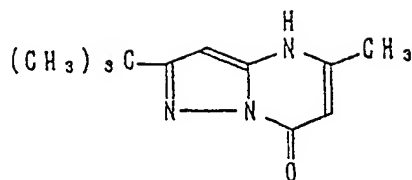
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Examples of the compounds represented by Formula III

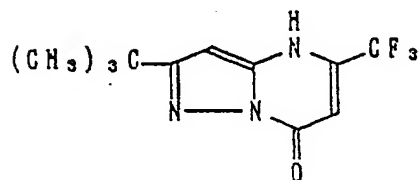
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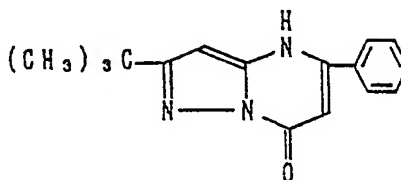
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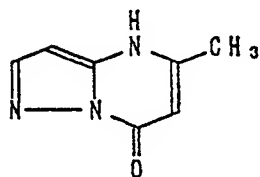
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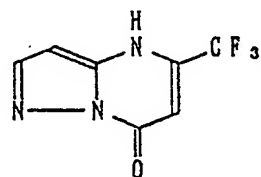
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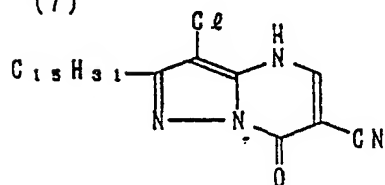
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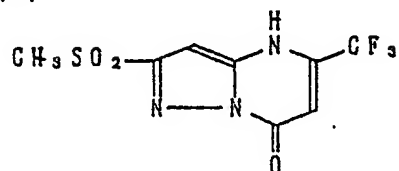
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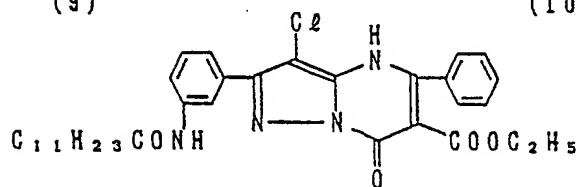
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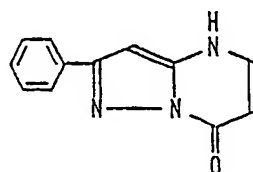
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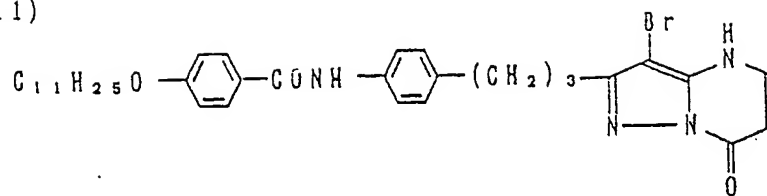
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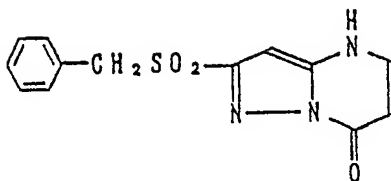
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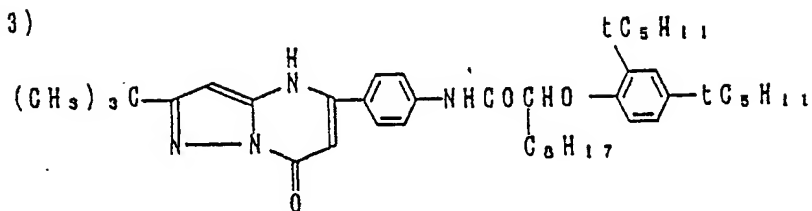
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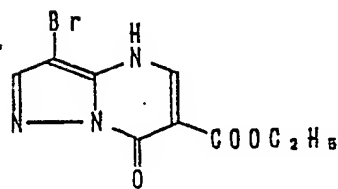
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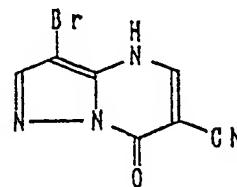
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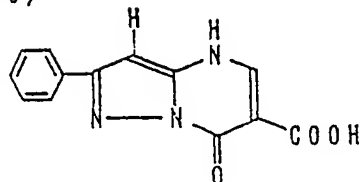
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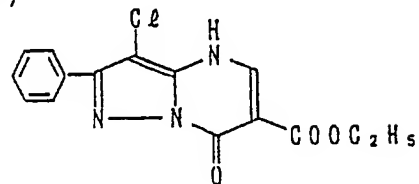
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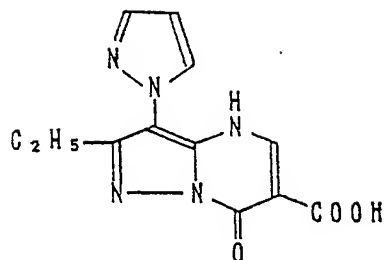
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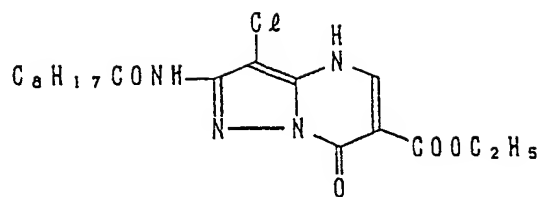
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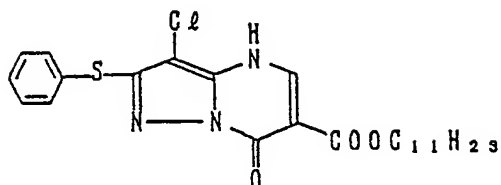
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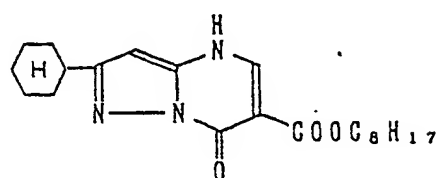
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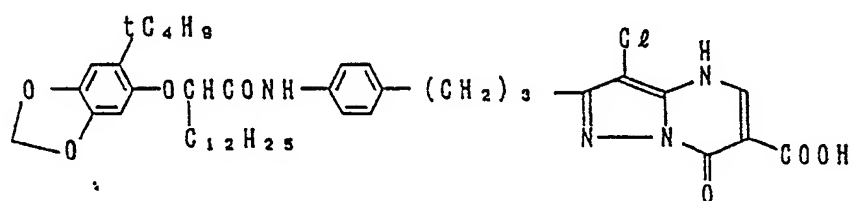
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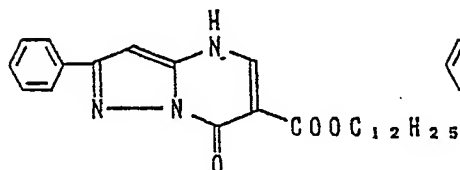
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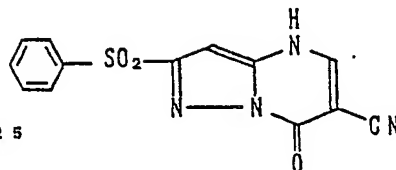
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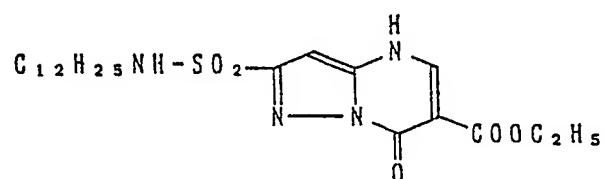
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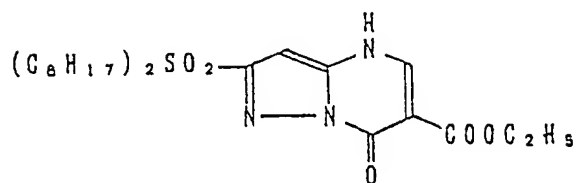


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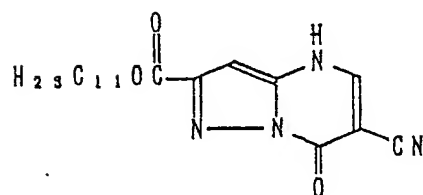




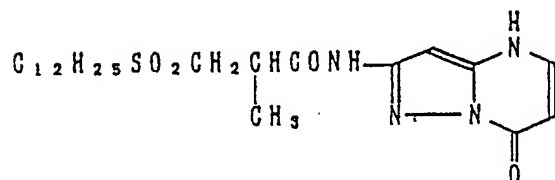
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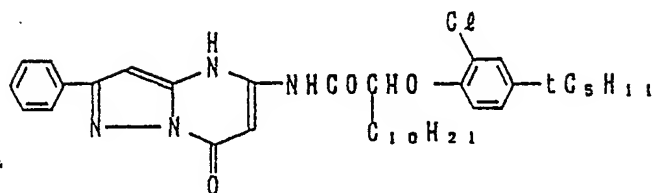
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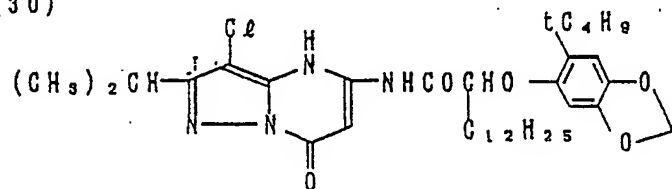
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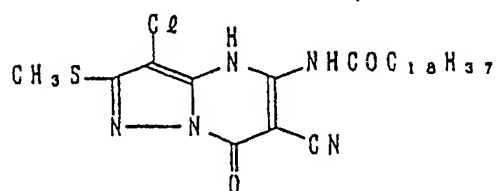
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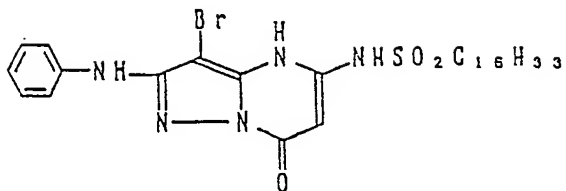
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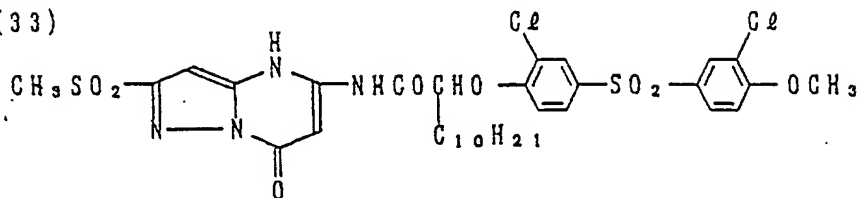
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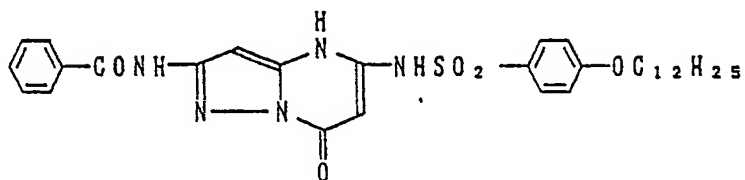
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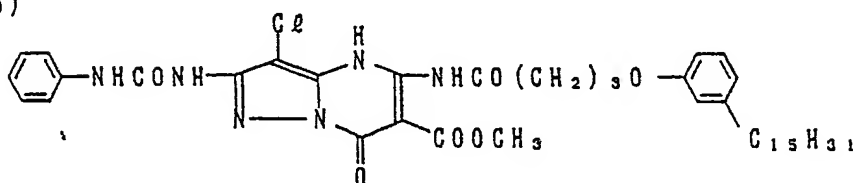
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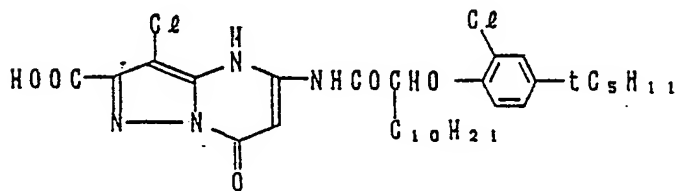
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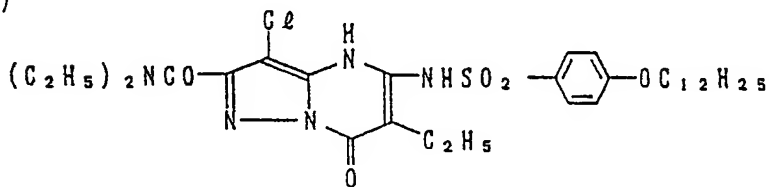
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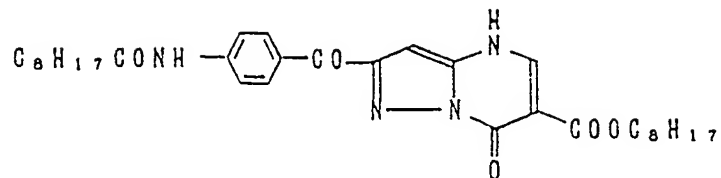
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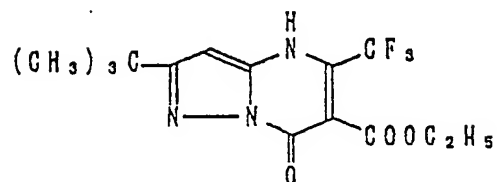
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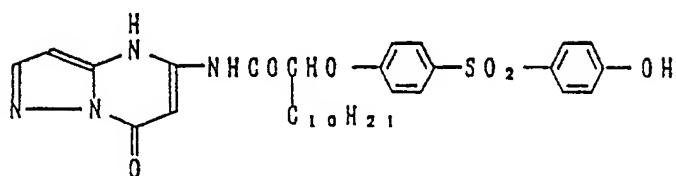
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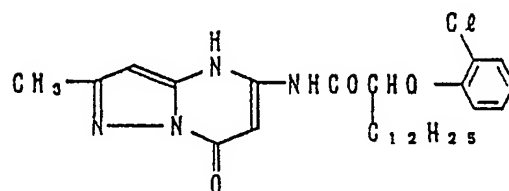
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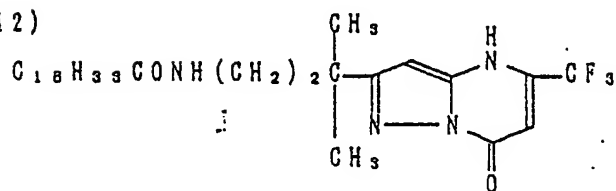
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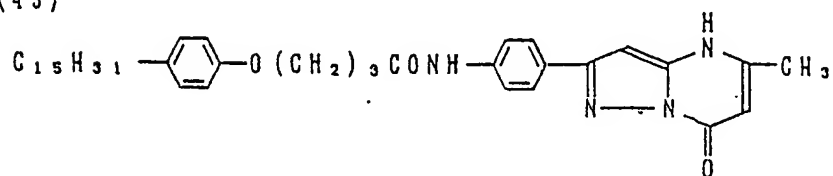
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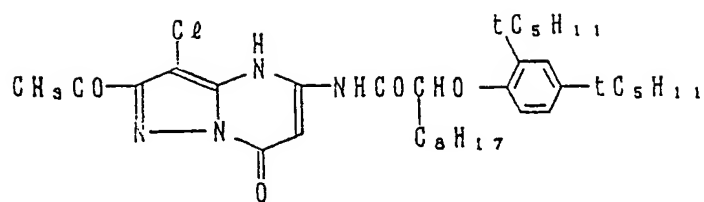
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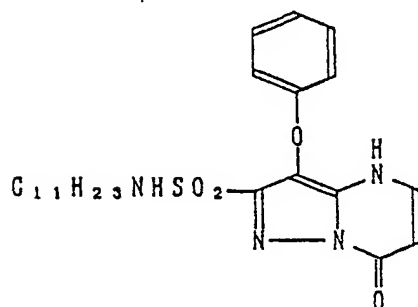
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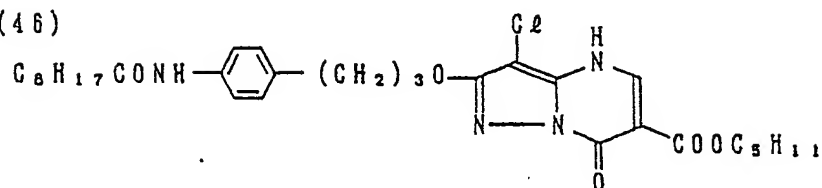
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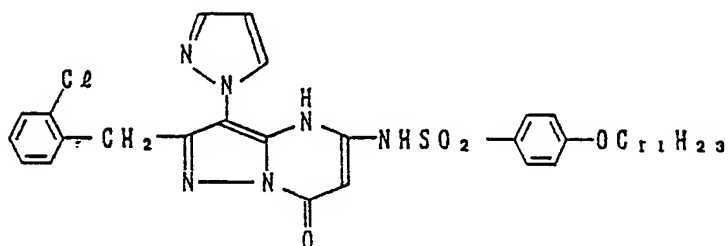
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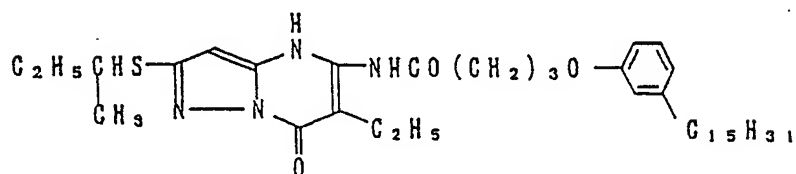
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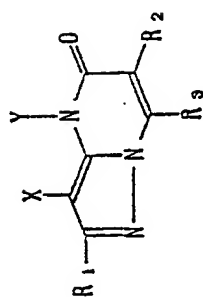
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(48)

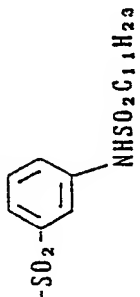
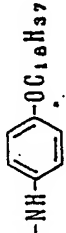
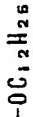
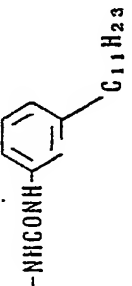
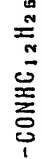

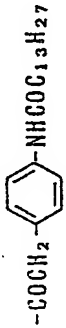





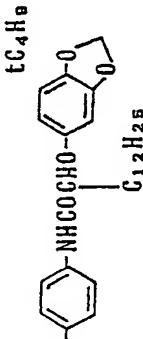

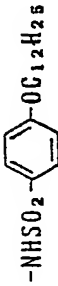
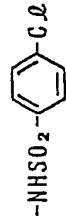
Examples of the compounds represented by Formula IV



No.	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	X
49	-CH <sub>3</sub>	H	H	C <sub>2</sub>
50	-C <sub>2</sub> H <sub>5</sub>	H	H	H
51	-C <sub>15</sub> H <sub>31</sub>	H	H	C <sub>2</sub>
52		H	H	H
53		H	H	C <sub>2</sub>
54		H	H	C <sub>2</sub>

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55		H	H	H
56		Br	H	H
57		Cl	H	H
58		H	H	H
59		Cl	H	H
60		H	H	H
61		Cl	H	H
62		H	-OH	-OH
63		H	-OC11H23	-OC11H23
64		Cl	-OC6H17	-OC6H17

No.	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	X
65		H	-OCH <sub>3</sub>	C <sub>2</sub>
66		H	-OC <sub>2</sub> H <sub>5</sub>	H
67	-C <sub>12</sub> H <sub>25</sub>	H	-OCH <sub>3</sub>	H
68	-COOC <sub>16</sub> H <sub>37</sub>	H	-OCH <sub>3</sub>	C <sub>2</sub>
69	H	C <sub>2</sub>	-CH <sub>3</sub>	C <sub>2</sub>
70	-SCH <sub>3</sub>	C <sub>2</sub>	-CH <sub>3</sub>	H
71		C <sub>2</sub>	-CH <sub>3</sub>	H
72		C <sub>2</sub>	-CH <sub>3</sub>	H

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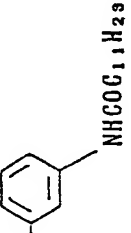
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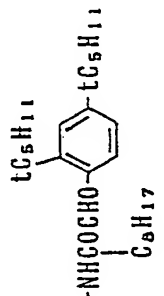
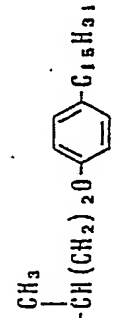
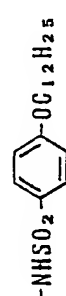
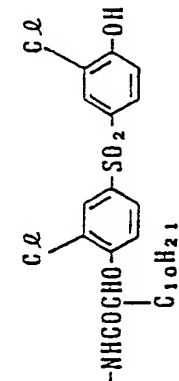
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73	$\begin{array}{c} \text{CH}_3 \\   \\ -\text{C}-\text{CH}_2\text{SO}_2\text{C}_{16}\text{H}_{33} \\   \\ \text{CH}_3 \end{array}$	C <sub>0</sub>	C <sub>0</sub>	-O-	-CH <sub>3</sub>
74	-C <sub>16</sub> H <sub>33</sub>	H	-C(CH <sub>3</sub> ) <sub>3</sub>		
75	-NHC <sub>6</sub> H <sub>5</sub>	Dr	-C <sub>11</sub> H <sub>23</sub>		H
76		C <sub>0</sub>	-CH <sub>3</sub>		H
77	$-\text{SO}_2\text{NH}-\text{C}_6\text{H}_4-\text{OC}-\text{C}_{11}\text{H}_{23}$	C <sub>0</sub>	-CH <sub>3</sub>		H
78	$-\text{CO}-\text{C}_6\text{H}_4-\text{C}_{11}\text{H}_{23}$	C <sub>0</sub>	-CH <sub>3</sub>		H



No	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	X
79	H	H	-NH <sub>2</sub> SO <sub>2</sub> C <sub>12</sub> H <sub>25</sub>	C <sub>2</sub>
80	-CH <sub>3</sub>	H		C <sub>2</sub>
81		H	-NHCOC <sub>4</sub> H <sub>9</sub>	H
82	-C(CH <sub>3</sub> ) <sub>3</sub>	H		C <sub>2</sub>
83	-C <sub>16</sub> H <sub>33</sub>	H		H

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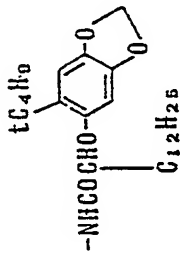
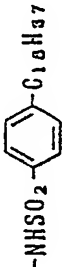

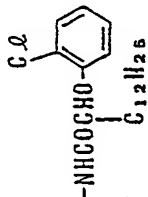
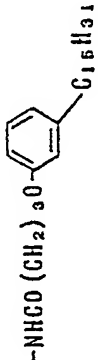
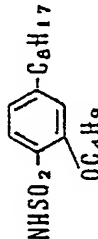
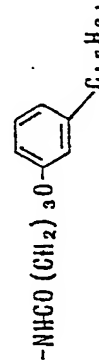
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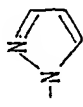
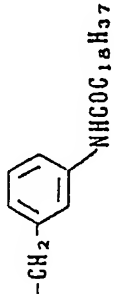
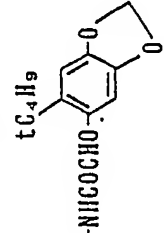
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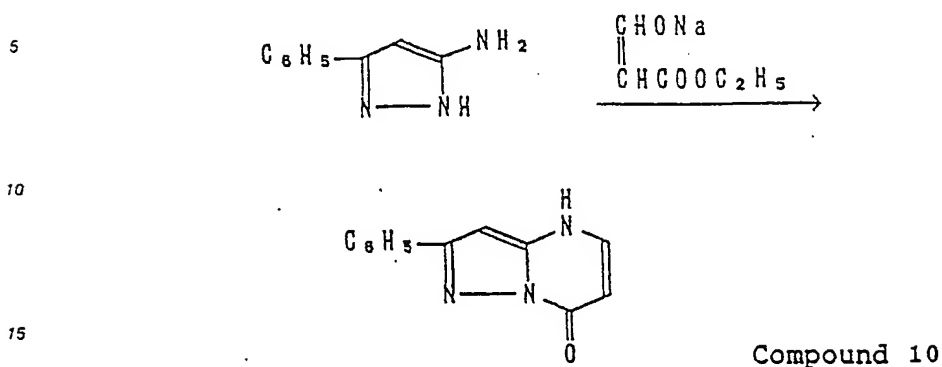
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84	$-\text{SO}_2\text{CH}_2\text{C}_6\text{H}_5$	H		H	$-\text{S}-\text{C}_6\text{H}_4-\text{OCH}_3$
85	$-\text{NHCOCH}_3$	H		H	
86		H		C.2	
87	$-\text{OC}_2\text{H}_5$	H		C.2	
88	$-\text{C}_6\text{H}_5$	H	$-\text{NHCOC}_{11}\text{H}_{23}$	H	
89	$-\text{SO}_2\text{N}(\text{C}_3\text{H}_7)_2$	H		H	
90	$-\text{SO}_2\text{NHC}_{12}\text{H}_{26}$	H		C.2	

No	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	X
91	-COOCH <sub>3</sub>	H	$\begin{array}{c} \text{-NHSO}_2\text{C}_{16}\text{H}_{33} \\ \text{tC}_5\text{H}_{11} \\ \text{-NHCOCHO-tC}_5\text{H}_{11} \\ \text{C}_{11}\text{H}_{23} \end{array}$	
92	-COCH <sub>3</sub>	H	$\begin{array}{c} \text{-NHSO}_2\text{C}_{16}\text{H}_{33} \\ \text{tC}_5\text{H}_{11} \\ \text{-NHCOCHO-tC}_5\text{H}_{11} \\ \text{C}_{11}\text{H}_{23} \end{array}$	H
93		H	-NHCOC <sub>2</sub> H <sub>5</sub>	C <sub>2</sub>
94	-CH <sub>3</sub>	-C <sub>2</sub> H <sub>5</sub>	$\begin{array}{c} \text{OC}_4\text{H}_9 \\ \text{-NHSO}_2\text{-C}_6\text{H}_{17} \\ \text{tC}_4\text{H}_9 \\ \text{-NHCOCHO-} \end{array}$	C <sub>2</sub>
95	-C <sub>6</sub> H <sub>5</sub>	-C <sub>6</sub> H <sub>17</sub>		H

Next, the typical synthesis examples of the compounds of the invention will be given below.

## Synthesis Example 1 (Synthesis of Compound 10)



20 In 150 ml (0.1 mol) of dehydrated ethanol, 15.9 g of 3-phenyl-5-aminopyrazole and 21.1 g (0.1 mol) of sodium ethylformyl acetate were refluxed with heating for 30 minutes. The reacted solution was filtrated with heating and the resulted filtrate was added with 500 ml of water. The pH of the solution was adjusted to be pH 1 to pH2 with diluted hydrachloric acid. The deposited crystals were filtrated. After the crystals were washed with water and then with ether, they were recrystallized, so that 5.28 g (0.025 mols) of white needle-shaped crystal compound No. 10 were obtained.

25 Melting point: 330 °C

IR: 1670, 950, 790, 760, 770, 530cm<sup>-1</sup>, <sup>1</sup>H-NMR(DMSO-d<sub>6</sub>); 12.3s broad (1H,NH), 7.95m (2H,H ortho), 7.85d(1H,H<sub>5</sub>, J<sub>5,6</sub> = 5Hz), 7.45m(3H,H meta and para), 6.62s(1H,H<sub>3</sub>), 5.71d(1H,H<sub>6</sub>)

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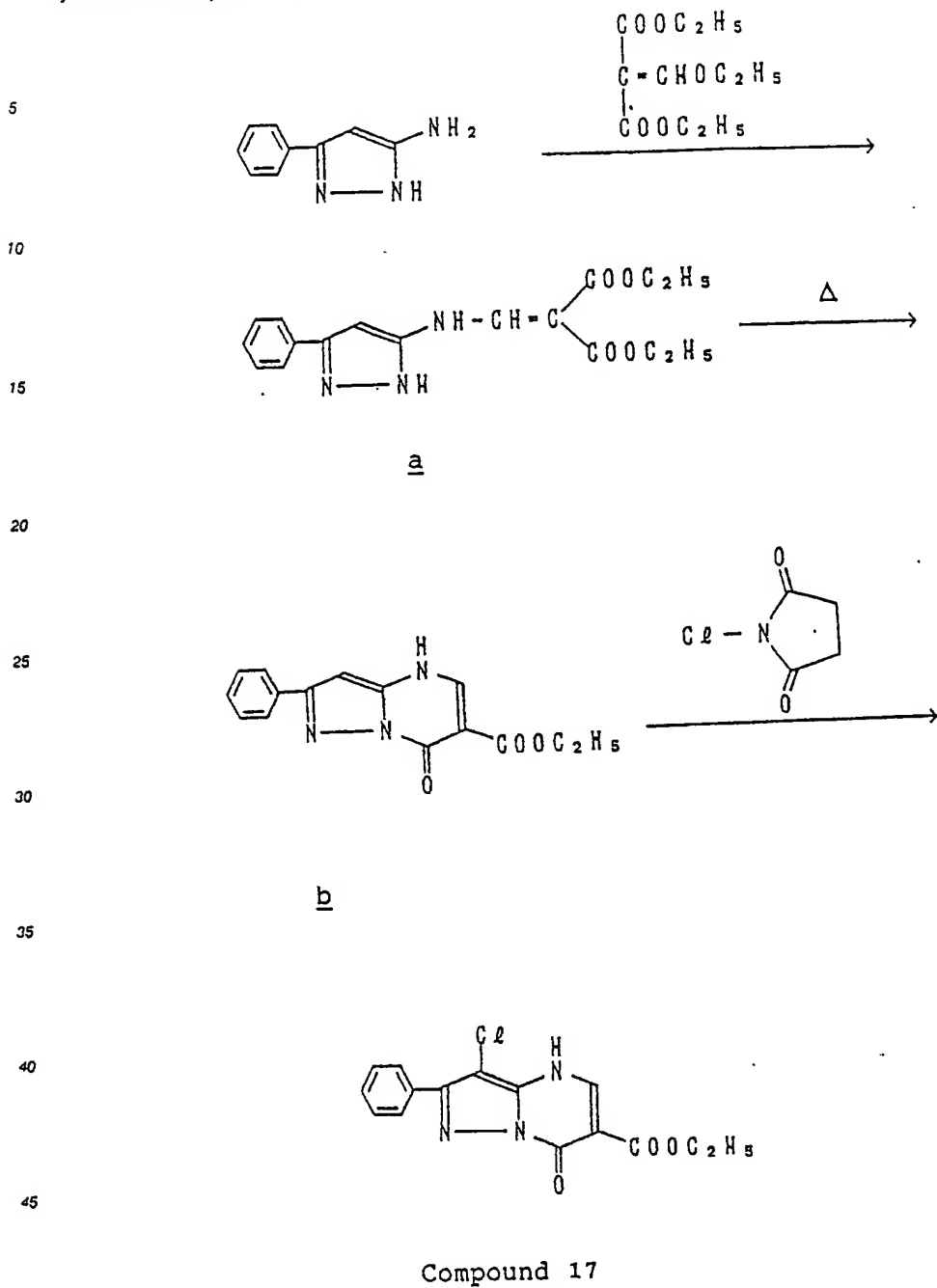
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## Synthesis Example 2 (Synthesis of Compound 17)



[Synthesis of a →]

In to 15.9 g (0.1 mol) of 3-phenyl-5-aminopyrazole, 43.2 g (0.2 mol) of diethylethoxymethylene malonate were added. The resulted oily mixture was stirred once and were then allowed to stand. The resulted solid matter was dissolved in 400 ml of ethanol and was then added with one liter of water gradually so as to filtrate the deposited white solid matter. The white solid matter was dissolved in benzene and was then recrystallized three times repeatedly by adding cyclohexane gradually to crystallize it, so that 19.1 g (0.058 mol) of a that was white needle-shaped crystals were obtained.

Melting point: 103 to 105 °C

IR: 3380, 3250, 1730, 1680, 1660, 1640, 1620, 1240, 795, 740 cm<sup>-1</sup>,

<sup>1</sup>H-NMR(CDCl<sub>3</sub>): 11.25 broad (1H, NH), 10.90d (1H, NH), 8.67d(1H, CH), 7.55m(2H, H ortho), 7.40m(3H, H meta and para), 6.25s(1H, H<sub>3</sub>)

15 [a → b]

A reaction vessel containing 16.4 g (0.05 mol) of a was heated at a temperature of 180 °C in an oil bath until a is melted and was then cooled down. The resulted solid matter was filtrated and washed with ethanol. The solid matter was recrystallized with dimethylformamide, so that 1.5 g (0.023 mol) of light-yellowish white crystals b were obtained.

Melting point: 302 to 304 °C

IR: 1715, 1430, 1300, 1175, 790, 690, 610 cm<sup>-1</sup>

<sup>1</sup>H-NMR(CF<sub>3</sub>COOH): 9.10<sub>s</sub>(1H, H<sub>5</sub>), 8.00m(2H, H ortho), 7.67m(3H, H meta or para), 7.21<sub>s</sub>(1H, H<sub>3</sub>)

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[b → Compound (17)]

b of 5.95 g (0.021 mol) were dissolved in 200 ml of chloroform and 3.0 g (0.022 mol) of N-chlorosuccinimide were then added thereto. The resulted solution was stirred for 30 minutes. The solvent was distilled off under reduced pressure and the remained matter was added with 150 ml each of ethyl acetate and water and was then extracted. After the ethyl acetate solution was dehydrated with magnesium sulfate, the extract was concentrated. The resulted concentrate was recrystallized with dimethylamide, so that 4.45 g (0.014 mol) of light-yellowish white needle-shaped crystals. i.e., Compound (17), was obtained.

FD-Mass-spectrum, M + 317

## 35 Elemental Analysis

Theoretical values, C:56.71, H:3.81, N:13.23, Cl:11.16

Measured values, C:56.79, H:3.75, N:13.28, Cl:11.22

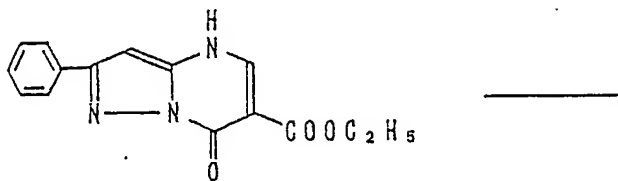
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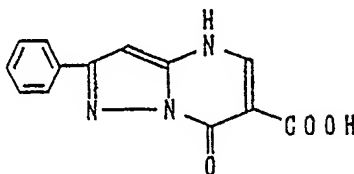
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## Synthesis Example 3 [Synthesis of Compound (16)]



(b of Synthesis Example 2)



Compound (16)

## [Synthesis of compound 16]

30 In a water-containing alcohol suspension of sodium hydroxide, 28.3 g (0.1 mol) of b which was synthesized in Synthesis Example 2 were heated until it was changed into a transparent solution and then refluxed. The reacted solution was adjusted to be pH 1 to 2 with diluted hydrochloric acid. The resulted white solid matter was filtrated and was then recrystallized with dimethylformamide, so that 13.0 g (0.051

35 mol) of white needle-shaped crystals, i.e., Compound (16), were obtained.

Melting point: Decomposition was found at 328 to 330 °C

FD-Mass spectrum, M+ 255

Elemental Analysis

Theoretical values, C:61.18, N:16.46, H:3.55

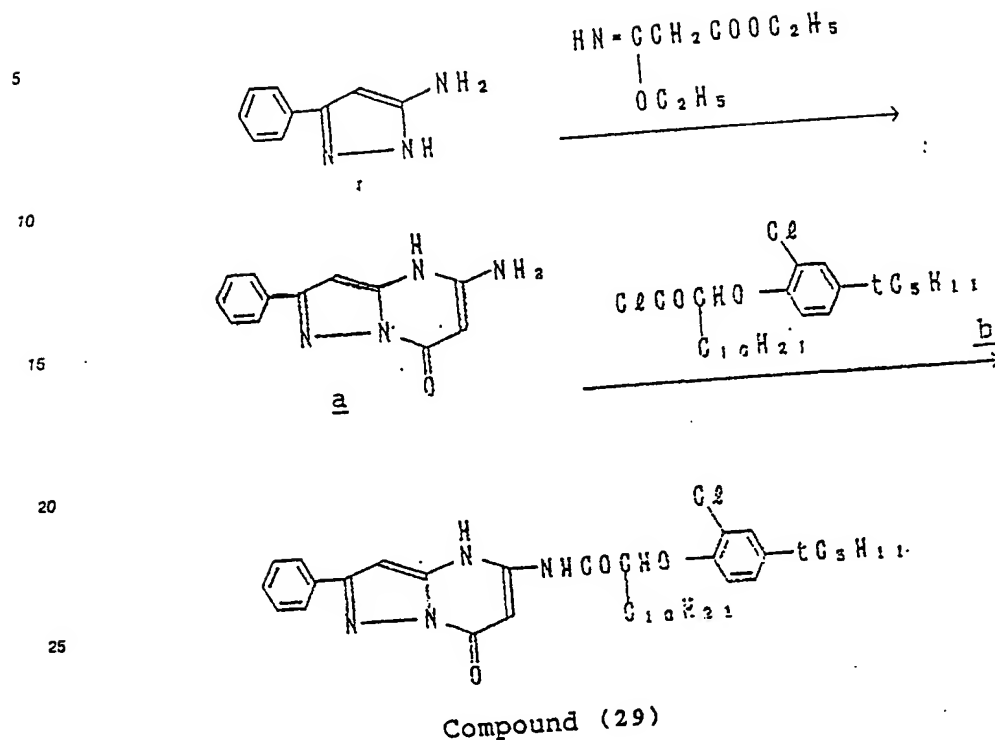
40 Measured values, C:61.05, N:16.58, H:3.50

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## Synthesis Example 4 (Synthesis of Compound 29)





FD-Mass spectrum:  $M^+ 604$

Elemental analysis

Theoretical values: C:69.446, H:7.49, N:9.26, Cl:5.86

Measured values: C:69.58, H:7.55, N:9.21, Cl:5.72

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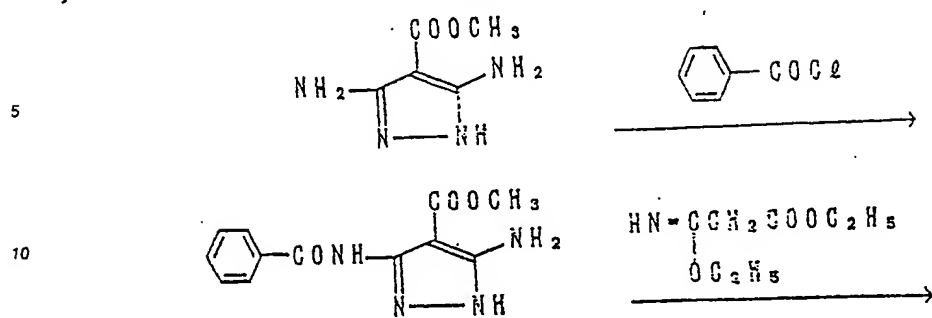
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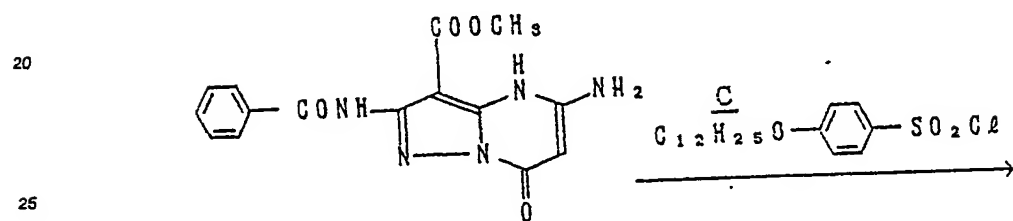
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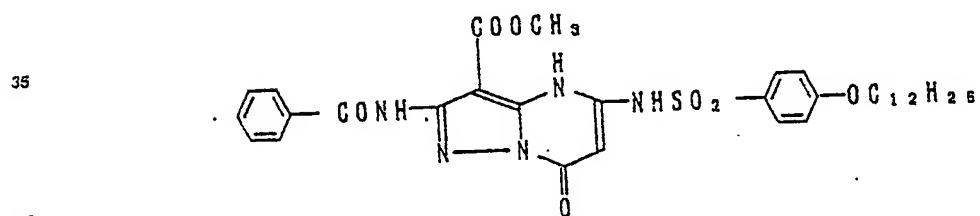
### Synthesis Example 5 [Synthesis of Compound (34)]



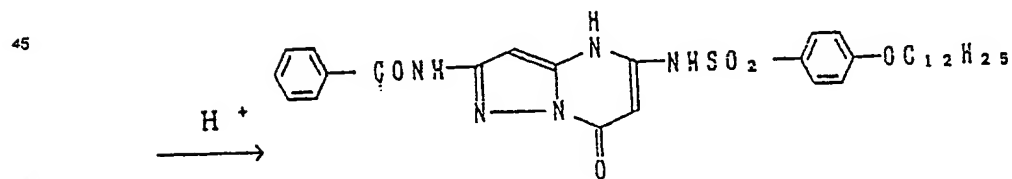
**a**



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Compound (34)

[Synthesis of a]

Into 500 ml of ethyl acetate were added with 15.6 g (0.1 mol) of methyl-3,5-diaminopyrazole-4-carboxylic acid, 14.1 g (0.1 mol) of benzoyl chloride and 15.2 g (0.15 mol) of triethylamine. The resulted solution was heated and refluxed for one hour. After the solution was cooled, the deposited crystals were  
 5 filtrated and then washed, so that 16.1 g (0.062 mol) of a were obtained.

[a - b]

10 As the materials of b, 16.0 g (0.062 mol) of a and 9.9 g (0.062 mol) of 2-ethoxycarbonylacetaoimidethyl ester were used. In the same manner as in [Synthesis of a] of the above-given Synthesis Example 4, b was synthesized by recrystallizing them with a mixed solvent of dimethylformamide and water, so that 13.1 g  
 (0.040 mol) of light-yellow needle-shaped crystals b were obtained.

15 FD-Mass spectrum:  $M^+$  327

Elemental analysis

Theoretical values: C:55.05, H:4.00, N:21.40

Measure values: C:54.95, H:4.08, N:20.35

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[b → d]

As the materials of d, 13.0 g (0.040 mol) of b and 14.4 g (0.040 mol) of c were used. In the same manner as in [a → Compound (29)] of Example 4, d was synthesized by recrystallizing with acetonitrile, so  
 25 that 16.9 g (0.026 mol) of d were obtained.

[d → Compound (34)]

30 d of 15.6 g (0.024 mol) were dissolved in 720 ml of a mixed solution of acetic acid, sulfuric acid and water in a proportion of 100:25:5. The resulted solution was refluxed with heating for one hour. After the resulted matter was adjusted to be pH5 with an aqueous sodium hydroxide solution, it was extracted with ethyl acetate and, the solvents were dehydrated with magnesium sulfate and distilled off. The residues were recrystallized with acetonitrile, so that 8.3 g (0.014 mol) of light-yellowish white needle-shaped crystals, i.e.,  
 35 Compound (34), were obtained.

FD-Mass spectrum  $M^+$  593

Elemental analysis

Theoretical values: C:62.71, H:6.62, N:11.80, S:5.40

Measure values: C:62.51, H:6.69, N:11.98, S:5.29

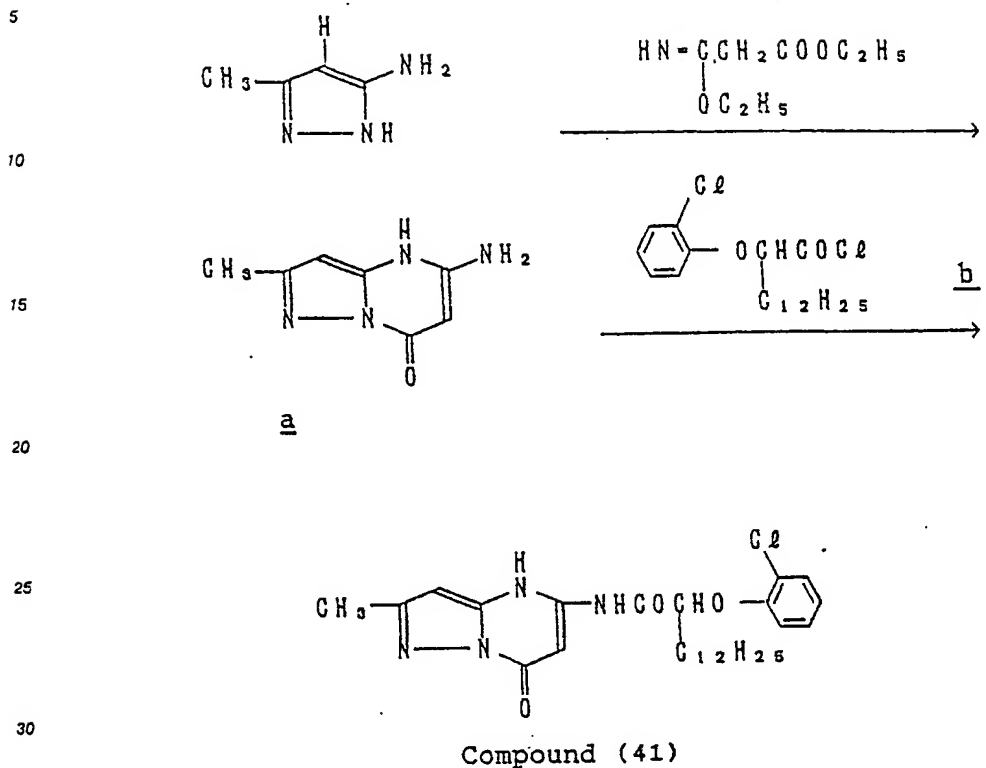
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## Synthesis Example 6 [Synthesis of Compound (41)]

35 [Synthesis of a]

By making use of 9.7 g (0.1 mol) of 5-amino-3-methylpyrazole and 15.9 g (0.1 mol) of 2-ethoxycarbonylacetamido ethyl ester, a was synthesized in the same manner as in Synthesis of a of Example 4 and a was recrystallized with a mixed solvent of dimethylformamide and water, so that 13.1 g (0.08 mol) of white

needle-shaped crystals of a were obtained.

Melting point: The decomposition was produced at a temperature of not lower than 300°C.

Elemental analysis

Theoretical values: C:51.21, N:34.13, H:4.91

Measured values: C:51.12, N:34.29, H:4.81

45 FD-Mass spectrum  $M^+$  164

$^1\text{H-NMR}$ (DMSO- $d_6$ ): 10.8 to 11.5 broad (1H, NH), 6.73 broad (2H,  $\text{NH}_2$ ), 5.82s(1H, H-3), 4.78s(1H, H-6), 2.25s-(3H,  $\text{CH}_3$ )

50 [a → Compound (41)]

By making use of 13.0 g (0.079 mol) of a and 29.5 g (0.079 mol) of b, Compound (41) was synthesized in the same manner as in [a → Compound (29)] of Synthesis Example 4 and was then recrystallized with acetonitrile, so that 21.5 g (0.043 mol) of white powder-like crystals, i.e., Compound (41), were obtained

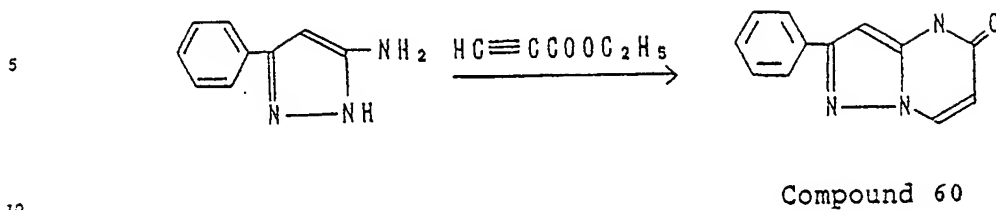
55 FD-Mass spectrum  $M^+$  500

Elemental analysis

Theoretical values: C:64.72, N:11.18, H:7.44, Cl:7.08

Measured values: C:64.92, N:11.21, H:7.38, Cl:7.00

## Synthesis Example 7 (Synthesis of Compound 60)



Into 130 ml of a dioxane solution containing 15.9 (0.1 mol) of 3-phenyl-5-aminopyrazole was added with 11.8 g (0.12 mol) of ethyl propionate and the resulted solution was refluxed with heating for 6 hours. The reacted solution was cooled and the deposited crystals were filtrated. The crystals were recrystallized with ethanol, so that 13.1 g (0.062 mol) of white needle-shaped crystals, i.e., Compound 60, were obtained. The melting point: 284 to 286 °C

IR: 1660, 950, 810, 780, 840, 680

<sup>1</sup>H-NMR(DMSO-d<sub>6</sub>): 12.12s(1H,NH), 8.50d(1H,H<sub>7</sub>), 7.90m(2H,H ortho), 7.40m(3H,H meta and para), 6.28s-(1H,H<sub>3</sub>), 5.95d(1H,H<sub>6</sub>)

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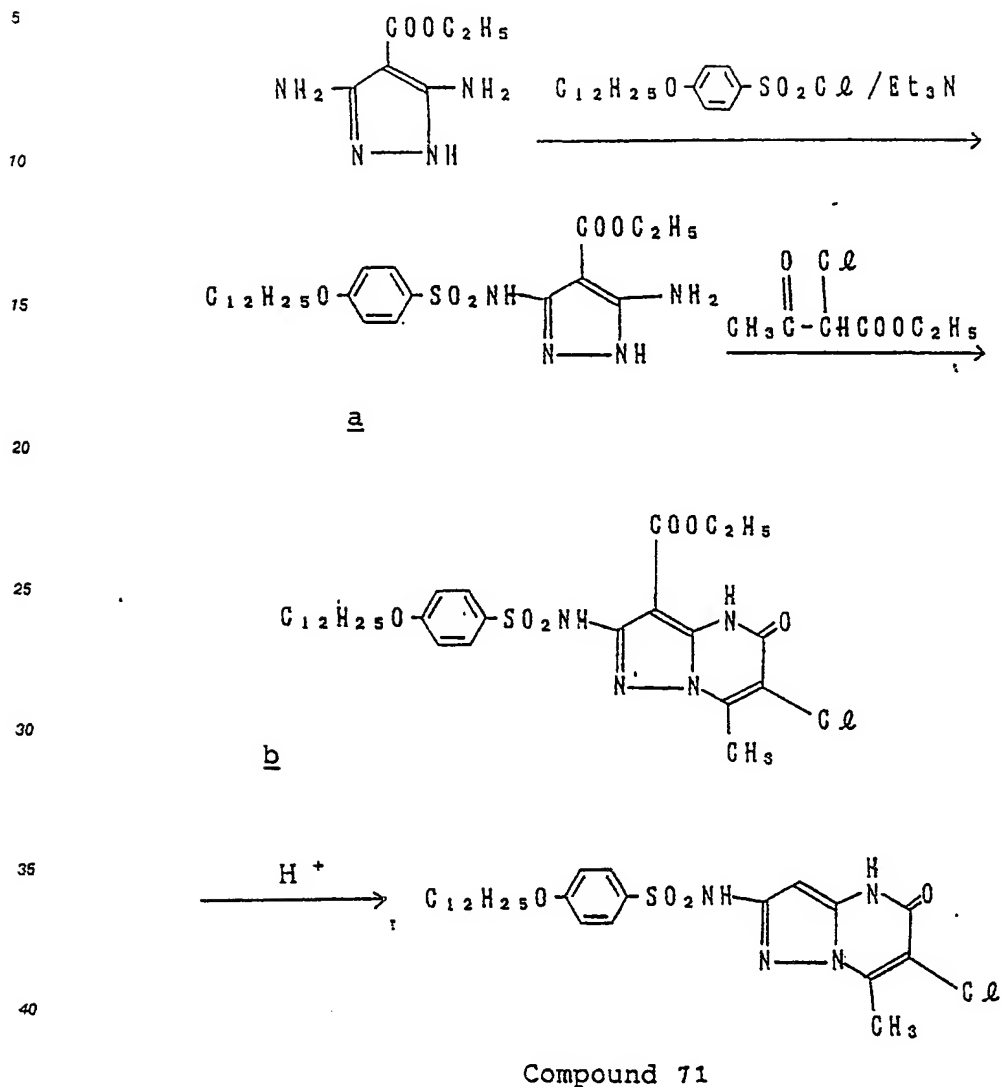
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## Synthesis Example 8 (Synthesis of Compound 71)

[Synthesis of a]

Into 500 ml of ethyl acetate were added with 17.0 g (0.1 mol) of ethyl-3,5-diaminopyrazole-4-carboxylic acid, 36.1 g (0.1 mol) of p-dodecylphenylsulfonyl chloride and 15.2 g (0.15 mol) of triethylamine. The resulted solution was refluxed with heating for one hour. After it was cooled down, the deposited crystals were filtrated and were then washed with water, so that 29.6 g (0.06 mol) of a were obtained.

[a → b]

In 600 ml of toluene, 29.1 g (0.059 mol) of a and 14.6 g (0.089 mol) of ethyl α-chloroaceto acetate were refluxed with heating for 6 hours and were then dehydrated.

5 The reacted solution was condensed under reduced pressure to obtain crude crystals. The crude crystals were recrystallized with ethanol, so that 16.1 g (0.027 mol) of white needle-shaped crystals, b, were obtained.

F-D mass spectrum 594

Elemental analysis

10 Theoretical values: C:56.51, N:9.41, Cl:5.96, S:5.39

Measure values: C:56.70, N:9.49, Cl:5.85, S:5.29

[b → Compound 71]

15

Into 130 ml of a mixed solvent of acetic acid, sulfuric acid and water (100:25:5), 15.4 g (0.026 mol) of b were dissolved. The resulted solution was refluxed with heating for one hour. The resulted matter was adjusted to be pH5 with sodium hydroxide and was then extracted with ethyl acetate. After the solvents were dehydrated with magnesium sulfate and were then distilled off. The residues were recrystallized with acetonitrile, so that 7.3 g (0.014 mol) of white needle-shaped crystals, i.e., Compound 71, were obtained.

20 F-d mass spectrum M<sup>+</sup> 522

Elemental analysis

Theoretical values: C:57.40, H:6.74, N:10.71, Cl:6.78, S:6.13

Measure values: C:57.65, H:6.82, N:10.60, Cl:6.59, S:6.08

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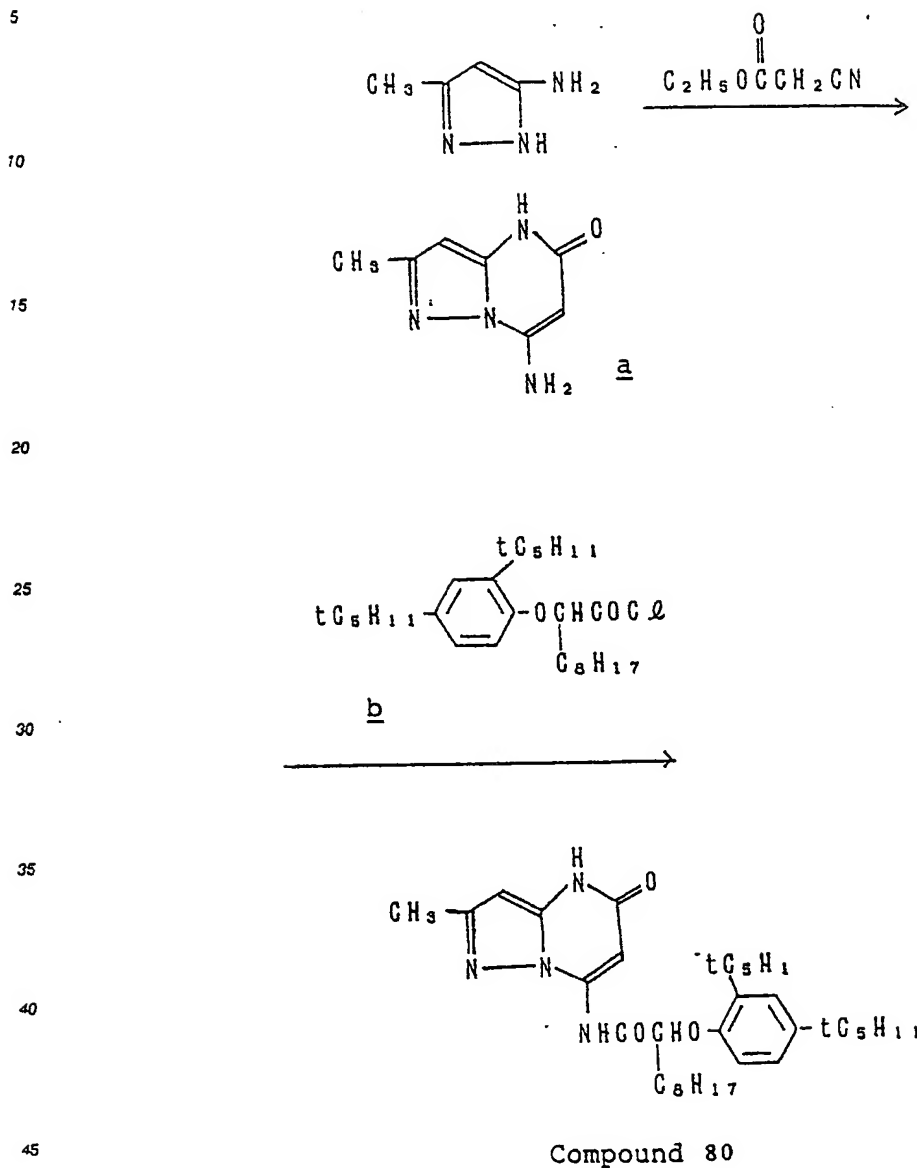
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## Synthesis Example 9 (Synthesis of Compound 80)

[Synthesis of a]

In 200 ml of dehydrated ethanol, 9.7 g (0.1 mol) of 5-amino-3-methylpyrazole and 11.3 g (0.1 mol) of ethyl cyanoacetate were refluxed with heating for 2.5 hours. After the reacted solution was cooled, the resulted precipitates were filtrated and were then washed with cooled ethanol. The precipitates were recrystallized with a mixed solvent of dimethyl formamide and water, so that 10.0 g (0.061 mol) of white powder a were obtained.



F-D mass spectrum  $M^+$  164  
 Elemental analysis  
 Theoretical values: C:51.21, N:34.13, H:4.91  
 Measure values: C:51.10, N:34.05, H:5.00

5

[a -- Compound 80]

Into 300 ml of an ethyl acetate solution containing 9.7 g (0.059 mol) of a were added with 80 ml of an  
 10 ethyl acetate solution containing 25.0 g (0.059 mol) of b and, further, with 6.14 g of triethylamine. The  
 resulted solution was stirred at room temperature for 2.5 hours and the deposited crystals were filtrated.  
 The crystals were washed with water and then recrystallized with acetonitrile, so that 16.5 g (0.030 mol) of  
 white powder, i.e., Compound 80, were obtained.

F-D mass spectrum  $M^+$  550

15 Elemental analysis

Theoretical values: C:71.96, N:10.17, H:9.15

Measured values: C:71.85, N:10.28, H:9.21

As exemplified by the above-given synthesis examples 1 through 9, the compounds of the invention  
 can be synthesized in an ordinary method by making use of a 3-substituted-5-aminopyrazole compound  
 20 having a variety of substituents in the third position, as the raw material.

Usually, the couplers of the invention may be used in an amount within the range of from  $1 \times 10^{-3}$  mol to  
 1 mol and, preferably, from  $1 \times 10^{-2}$  mol to  $8 \times 10^{-1}$  mol per mol of silver halide used.

The couplers of the invention are also allowed to be used with other kinds of couplers in combination.

To the couplers of the invention, it is similarly allowed to apply ordinary methods and techniques  
 25 applicable to normal types of dye-forming couplers.

The couplers of the invention can also be used as a material of color photographs finished in any color  
 forming methods. Such color forming methods include, more typically, a non-incorporated coupler type  
 color forming method and an incorporated coupler type color forming method. When using the couplers of  
 the invention in the non-incorporated coupler type color forming method, the couplers of the invention may  
 30 be used by dissolving them in either an aqueous alkaline solution or an organic solvent such as alcohol or  
 the like and then by adding them into a color developing solution.

When using the couplers of the invention as a material of color photographs finished in the incorporated  
 coupler type color forming method, the couplers of the invention may be used by adding them into a  
 photographic light-sensitive material.

35 Typically, it is preferable to use such a method that the couplers of the invention are compounded into  
 a silver halide emulsion and the emulsion is coated on a support to produce a color light-sensitive material.  
 The couplers of the invention may be used in such a color photographic light-sensitive material as color-  
 negative and color-positive films, color-print papers and so forth.

The light-sensitive materials including the above-mentioned color-print papers, in which the couplers of  
 40 the invention are used, may be those for monochrome or multicolor use. In such a multicolor light-sensitive  
 material, the couplers of the invention may be contained in any layers thereof. It is, however, usual to  
 contain the couplers into a red light-sensitive silver halide emulsion layer. Such multicolor light-sensitive  
 materials have dye image forming component units which are sensitive to three primary spectral color  
 regions, respectively. Each of the component units may be comprised of a single or multiplied emulsion  
 45 layer sensitive to a certain spectral region. In a light-sensitive material, the component layers including the  
 image forming component unit layer may be arranged in various order as known in the art.

A typical multicolor light-sensitive material of the invention comprises a support carrying thereon a cyan  
 dye image forming component unit comprising at least one red sensitive silver halide emulsion layer  
 containing at least one cyan coupler out of which at least one of them is the cyan coupler of the invention, a  
 50 magenta dye image forming component unit comprising at least one green sensitive silver halide emulsion  
 layer containing at least one magenta coupler and a yellow dye image forming component unit comprising  
 at least one blue sensitive silver halide emulsion layer containing at least one yellow coupler, respectively.

The light-sensitive materials are also allowed to have additional layers such as a filter layer, an  
 interlayer, a protective layer, a subbing layer and so forth. In order to contain the couplers of the invention  
 55 into an emulsion, it is allowed to follow the conventionally known methods. For example, the couplers of the  
 invention are dissolved independently or in combination in a high boiling organic solvent having a boiling  
 point of not lower than  $175^\circ\text{C}$  such as tricresyl phosphate, dibutyl phthalate or the like or in a low boiling  
 solvent such as butyl acetate, butyl propionate or the like, or in the mixed solvent thereof if required. The

resulted solution is mixed with an aqueous gelatin solution containing a surfactant and the mixture thereof is then emulsified by making use of a high-speed rotary mixer or a colloid-mill. After then, the resulted dispersion is added into a silver halide emulsion, so that a silver halide emulsion applicable to the invention may be prepared.

- 5 To a light-sensitive material containing the coupler of the invention, the silver halide compositions which should preferably be applicable include, for example, silver chloride, silver chlorobromide or silver chloriodobromide. The compositions thereof may also be a combined mixture of a mixture of silver chloride and silver bromide or the like. When a silver halide emulsion is to be used in a color-print paper, for example, a rapid developability is particularly required. The silver halide emulsion should, therefore, be  
 10 preferred to contain chlorine atom as the halide composition of the silver halide. The particularly preferable silver halide compositions include silver chloride, silver chlorobromide or silver chloriodobromide each having a silver chloride content of at least 1%.

The silver halide emulsions may be chemically sensitized in an ordinary method, and it may also be optically sensitized to a desired wavelength range.

- 15 The silver halide emulsions may also be added with a compound which is known in the photographic art as an antifoggant or a stabilizer, with the purposes of preventing fogging and/or keeping photographic stability in the course of manufacturing, storing or processing a light-sensitive material.

- The color light-sensitive materials containing the couplers of the invention may further be applied with a color-fog inhibitor, a dye image stabilizer, a UV absorbent, an antistatic agent, a matting agent, a surfactant  
 20 and so forth each of which is commonly used in light-sensitive materials.

For further details of these additives, it may be referred to Research Disclosure, Vol. 176, pp. 22 to 31, December, 1978, for example.

With a color photographic light-sensitive material containing the couplers of the invention, an image may be formed through a color developing process which is well-known in the art.

- 25 The color photographic light-sensitive materials used therein the couplers relating to the invention are allowed to contain a color developing agent as itself or its precursor in the hydrophilic colloidal layers of the light-sensitive materials so as to be processed in an alkaline activating bath.

- The color photographic light-sensitive materials used therein the couplers of the invention may be color-developed, bleached and then fixed, provided that the bleaching step and the fixing step may be carried out  
 30 at the same time.

After the fixing step, a washing step is commonly be carried out. It is, however, allowed to carry out either a stabilizing step in place of the washing step, or the process combined with these two steps.

## 35 Examples

Next, the invention will be described further in detail with reference to the examples. It is, however, to be understood that the invention shall not be limited thereto.

40

### Example 1

- 45 The following layers were coated on a paper support laminated on the both sides with polyethylene, in order from the support side, so that Sample 1 of a red color light-sensitive material was prepared. Unless otherwise expressly stated, the amounts of the compounds added will be shown as an amount per square meter. (An amount of silver halide will be shown in terms of silver.)

50

Layer 1: An emulsion layer

- A red-sensitive emulsion layer comprising 1.2 g of gelatin, 0.30 g of a red-sensitive silver chlorobromide emulsion (having a silver chloride content of 96 mol%), and  $9.1 \times 10^{-4}$  mol of Comparative Cyan Coupler a  
 55 dissolved in 1.35 g of dioctyl phosphate

## Layer 2: A protective layer

A protective layer containing 0.50 g of gelatin. This layer was also added with sodium salt of 2,4-dichloro-6-hydroxy-s-triazine in an amount of 0.017 g per g of gelatin, as a hardener.

5 Next, Samples 2 through 15 of the invention were prepared in exactly the same manner as in Sample 1, except that Comparative Coupler a was replaced by the coupler indicated in Table 1 (of which the amount added was the same mol amount as that of Comparative Coupler a).

Thus prepared Samples 1 through 15 were exposed to light in an ordinary method and were then processed in the following steps, respectively.

10

## Processing steps:

15

Color developing	38 ° C	3 min. 30 sec.
Bleach-fixing	38 ° C	1 min. 30 sec.
Stabilizing or washing	25 to 30 ° C	3 min.
Drying	75 to 80 ° C	2 min.

20

In the above-given processing steps, the composition of each processing solution was as follows.

## Color developer:

25

Benzyl alcohol 15 ml  
 Ethylene glycol 15 ml  
 Potassium sulfite 2.0 g  
 Potassium bromide 0.7 g  
 30 Sodium chloride 0.2 g  
 Potassium carbonate 30.0 g  
 Hydroxylamine sulfate 3.0 g  
 Polyphosphoric acid (TPPS) 2.5 g  
 3-methyl-4-amino-N-ethyl-N-( $\beta$ -methanesulfonamidoethyl)aniline sulfate 5.5 g  
 35 Fluorescent brightening agent (A 4,4'-diaminostilbenedisulfonic acid derivative) 1.0 g  
 Potassium hydroxide 2.0 g  
 Add water to make a total of 1 liter  
 Adjust pH to be pH 10.20

40

## Bleach-fixer:

Ferric ammonium ethylenediaminetetraacetate, dihydrate 60 g  
 45 Ethylenediaminetetraacetate 3 g  
 Ammonium thiosulfate (In a 70% solution) 100 ml  
 Ammonium sulfite (In a 40% solution) 27.5 ml  
 Adjust pH with potassium carbonate or glacial acetic acid to be pH 7.1  
 Add water to make a total of 1 liter

50

## Stabilizer:

55 5-chloro-2-methyl-4-isothiazoline-3-one 1.0 g  
 Ethylene glycol 10g  
 Add water to make 1 liter

With respect to Samples 1 through 15 thus processed, the density of each sample was measured with a densitometer, Model KD-7 manufactured by Konishiroku Photo Ind. Co., Ltd. and, further, each of the samples was allowed to stand for 14 days in an atmosphere of a high temperature and a high humidity (at 60°C and 80%RH) and, then, the resistance against heat and moisture of dye images were checked up.

Further, each of the samples was irradiated for 10 days by a Xenon in Fade-o-meter and, then, the density of the samples were measured and the light fastness thereof were checked up. The results thereof are shown in Table 1, provided that the heat resistance, moisture resistance and light fastness of dye images are expressed by a percentage of the residual dye density obtained after the tests of resistance against heat, moisture and light to the initial density of 1.0.

Comparative Coupler a

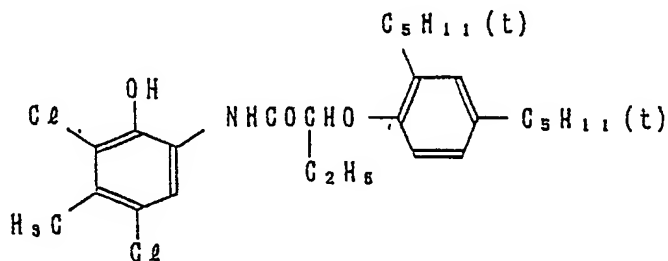


Table 1

Sample No.	Coupler used	Residual ratio of dye (%)	
		Heat/Moisture resistance	Light-fastness
1	Comp. a	60	84
2	Inv. 9	95	85
3	Inv. 11	90	80
4	Inv. 13	94	81
5	Inv. 19	91	90
6	Inv. 29	92	83
7	Inv. 42	95	79
8	Inv. 43	92	89
9	Inv. 49	91	82
10	Inv. 53	88	85
11	Inv. 67	90	83
12	Inv. 71	91	85
13	Inv. 73	90	88
14	Inv. 82	94	85
15	Inv. 88	93	82

As is obvious from the results shown in Table 1, it is found that every samples used therein the couplers of the invention are high in dye residual ratio, excellent in both heat and moisture resistance without degradation in light-fastness, as compared to the sample used therein the comparative coupler.

## Example 2

Onto a subbed triacetate film support was coated with each of the following layers in order from the support, so that a red color light-sensitive material sample No. 16 was prepared. The amount of each compound added will be expressed in terms of an amount added per square meter unless otherwise expressly stated. (provided that an amount of silver halide added will be expressed in terms of silver.)

Layer 1: An emulsion layer

A red-sensitive emulsion layer comprising 1.3 g of gelatin, 1.5 g of a red-sensitive silver iodobromide emulsion (having a silver iodide content of 4 mol%), and  $8.0 \times 10^{-4}$  mol of Comparative Cyan Coupler b dissolved in 1.1 g of tricresyl phosphate

15

Layer 2: A protective layer

A protective layer containing 1.5 g of gelatin. This layer was also added with sodium salt of 2,4-dichloro-6-hydroxy-s-triazine in an amount of 0.017 g per g of gelatin, as a hardener.

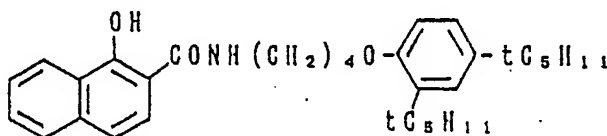
Next, Samples 17 through 29 of the invention were prepared in exactly the same manner as in Sample 16, except that Comparative Coupler b was replaced by the coupler indicated in Table 2 (of which the amount added was the same mol amount as that of Comparative Coupler b).

Thus prepared film samples were exposed to light in an ordinary method and were then color developed in the following color processing steps, respectively.

25

Comparative coupler b

30



35

Processing steps: Processing temperature at 38°C

40

45

50

	Processing time
Color developing	3 min. 15 sec.
Bleaching	6 min. 30 sec.
Washing	3 min. 15 sec.
Fixing	6 min. 30 sec.
Washing	3 min. 15 sec.
Stabilizing	1 min. 30 sec.
Drying	

In the above-given processing steps, the composition of each processing solution was as follows.

55

## Color developer:

- 4-amino-3-methyl-N-ethyl-N-( $\beta$ -hydroxyethyl)aniline sulfate 4.75 g  
 Sodium sulfite, anhydrous 4.25 g  
 5 Hydroxyamine 1/2 sulfate 2.0 g  
 Potassium carbonate, anhydrous 37.5 g  
 Sodium bromide 1.3g  
 Trisodium nitrilotriacetate, monohydrate 2.5 g  
 Potassium hydroxide 1.0 g  
 10 Add water to make 1 liter  
 Adjust pH with sodium hydroxide to be pH10.6

## 15 Bleaching solution:

- Ferric-ammonium ethylenediaminetetraacetate 100.0 g  
 Diammonium ethylenediaminetetraacetate 10.0 g  
 Ammonium bromide 150.0 g  
 20 Glacial acetic acid 10.0 g  
 Add water to make 1 liter  
 Adjust pH with aqueous ammonia to be pH6.0

25

## Fixer:

- Ammonium thiosulfate 175.0 g  
 Sodium sulfite, anhydrous 8.0 g  
 30 Sodium metasulfite 2.3 g  
 Add water to make 1 liter  
 Adjust pH with acetic acid to be pH6.0

35

## Stabilizer:

- Formalin (at 37 wt%) 1.5 ml  
 Koniducks (manufactured by Konishiroku Photo Ind. Co., Ltd.) 7.5 ml  
 40 Add water to make 1 liter

With respect to Samples 16 through 29 thus processed, the density of cyan images formed on each sample was measured with a densitometer, Model KD-7 manufactured by Konishiroku Photo Ind. Co., Ltd. and, further, each of the samples was allowed to stand for 14 days in an atmosphere of a high temperature and a high humidity (at 60°C and 80%RH) and, then, the resistance against heat and moisture of dye  
 45 images were checked up.

Further, each of the samples was irradiated for 10 days by a Xenon in Fade-o-meter and, then, the density of the samples were measured and the light fastness thereof were checked up.

The results thereof are shown in Table 2, provided that the heat resistance, moisture resistance and  
 50 light fastness of dye images are expressed by a percentage of the residual dye density obtained after the tests of resistance against heat, moisture and light to the initial density of 1.0.

55

Table-2

Sample No.	Coupler used	Residual ratio of dye (%)	
		Heat/Moisture resistance	Light-fastness
16	Comp. b	71	80
17	Inv. 25	91	85
18	Inv. 27	92	86
19	Inv. 33	85	83
20	Inv. 37	91	85
21	Inv. 38	92	84
22	Inv. 44	90	81
23	Inv. 55	84	80
24	Inv. 59	88	82
25	Inv. 68	92	80
26	Inv. 78	86	83
27	Inv. 84	93	85
28	Inv. 90	91	82
29	Inv. 92	89	85

As is obvious from the results shown in Table 2, it is found that every samples used therein the couplers of the invention are high in dye residual ratio, excellent in both heat and moisture resistance without degradation in light-fastness, as compared to the sample used therein the comparative coupler.

### Example 3

Onto a triacetyl cellulose film support was coated with each of the following layers in order from the support, so that red color light-sensitive reversal photographic material samples No. 30 through No. 40 were prepared.

#### Layer 1: An emulsion layer

A red-sensitive emulsion layer comprising 1.4 g of relating 0.5 g of a red-sensitive silver chlorobromide emulsion (having a silver chloride content of 96 mol%), and  $9.1 \times 10^{-4}$  mol of the coupler dissolved in 1.5 g of dibutyl phthalate.

#### Layer 2: A protective layer

A protective layer containing 0.5 g of gelatin. This layer was also added with sodium salt of 2,4-dichloro-6-hydroxy-s-triazine in an amount of 0.017 g per g of gelatin, as a hardener.

Thus prepared samples were exposed to light in an ordinary method and were then developed in the following steps, respectively.

#### Reversal Processing Steps:

Step	Time	Temperature
First developing	6 min.	38° C
Washing	2 min.	38° C
Reversing	2 min.	38° C
Color developing	6 min.	38° C
Adjusting	2 min.	38° C
Bleaching	6 min.	38° C
Fixing	4 min.	38° C
Washing	4 min.	38° C
Stabilizing	1 min.	38° C
Drying		At an ordinary temperature

The compositions of the processing solutions used were as follows.

First developer:

Sodium tetrapolyphosphate 2 g  
 Sodium sulfite 20 g  
 Hydroquinone monosulfonic acid 30 g  
 Sodium carbonate, monohydrate 30 g  
 1-phenyl-4-methyl-4-hydroxymethyl-3-pyrazolidone 2 g  
 Potassium bromide 2.5 g  
 Potassium thiocyanate 1.2 g  
 Potassium iodide (in a 0.1% solution) 2 ml  
 Add water to make 1000 ml

Reversing solution:

Hexasodium nitrilotrimethylenephosphonate 3g  
 Stannous chloride, dihydrate 1 g  
 p-aminophenol 0.1g  
 Sodium hydroxide 5 g  
 Glacial acetic acid 15 ml  
 Add water to make 1000 ml

Color developer:

Sodium tetrapolyphosphate 2 g  
 Sodium sulfite 7 g  
 Tertiary sodium phosphate, 12 hydrate 36 g  
 Potassium bromide 1g  
 Potassium iodide (in a 0.1% solution) 90 ml  
 Sodium hydroxide 3g  
 Citrazinic acid 1.5 g  
 N-ethyl-N-( $\beta$ -methanesulfonamidoethyl)-3-methyl-4-aminoaniline sulfate 11 g  
 Ethylenediamine 3 g  
 Add water to make 1000 ml



## Adjusting solution:

Sodium sulfite 12 g  
 Sodium ethylenediaminetetraacetate, dihydrate 8 g  
 5 Thioglycerol 0.4 ml  
 Glacial acetic acid 3 ml  
 Add water to make 1000ml

10

## Bleaching solution:

Sodium ethylenediaminetetraacetate, dihydrate 2.0 g  
 Ferric ammonium ethylenediaminetetraacetate, dihydrate 120.0 g  
 15 Potassium bromide 100.0 g  
 Add water to make 1000 ml

20 Fixer:

Ammonium thiosulfate 80.0 g  
 Sodium sulfite 5.0 g  
 Sodium bisulfite 5.0 g  
 25 Add water to make 1000 ml

## Stabilizer:

30

Formalin (at 37 wt%) 5.0 ml  
 Koniducks (manufactured by Konishiroku Photo Ind. Co., Ltd.) 5.0 ml  
 Add water to make 1000 ml

35 With respect to each of the samples thus processed, the resistance against heat and moisture and light-fastness of the cyan dye images were examined in the same manner as in Example 2. The results thereof are shown in Table-3.

Table-3

40

45

50

55

Sample No.	Coupler used	Residual ratio of dye (%)	
		Heat/Moisture resistance	Light-fastness
30	Comp. a	61	85
31	Inv. 7	92	89
32	Inv. 23	94	87
33	Inv. 28	91	84
34	Inv. 30	93	86
35	Inv. 32	92	85
36	Inv. 51	91	82
37	Inv. 64	90	84
38	Inv. 76	88	83
39	Inv. 81	90	83
40	Inv. 85	93	84

As is obvious from the results shown in Table-3, it is found that every samples used therein the couplers of the invention are high in dye residual ratio, excellent in both heat and moisture resistance and without degradation in light-fastness, as compared to the sample used therein the comparative coupler.

In conclusion, it is found that the dye images formed with the couplers of the invention are resistive  
5 against heat, moisture and light.

### Claims

- 10 1. A coupler for photographic material represented by the following Formula I.  
Formula I



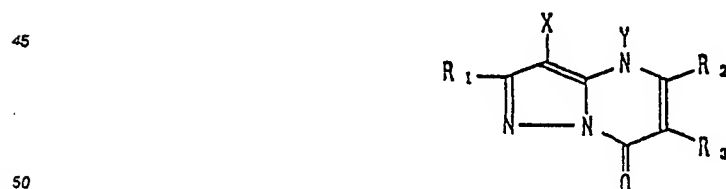
- 20 wherein Z is a group of non-metal atoms necessary for completing a nitrogen-containing six-member heterocyclic ring condensed with the pyrazole ring of Formula I, said six-member ring may be substituted or not substituted provided that said six-member ring does not be condensed with any other ring than said pyrazole ring; R represents a hydrogen atom or a substituent, and X represents a hydrogen atom or a substituent capable of being split off upon reaction with the oxidized product of a color developing agent.

- 25 2. The coupler of claim 1, wherein said coupler is represented by the following Formula II; Formula II



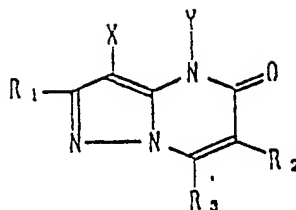
- 35 wherein Z1 represents a group of non-metal atoms necessary to complete a nitrogen-containing six-member ring condensed with the pyrazole ring of Formula II, said six-member ring contains an -NY- group and a carbonyl group and does not be condensed with any other ring than said pyrazole ring; Y represents a hydrogen atom or a substituent; and R and X are synonymous with R and X denoted in Formula I, respectively.

- 40 3. The coupler of claim 2, wherein said coupler is represented by the following Formula III; Formula III;



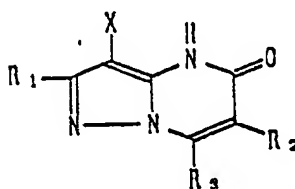
- 55 wherein R1, R2, and R3 each are synonymous with R denoted in Formula I, provided that R2 is not a hydroxy group; X and Y are synonymous with X denoted in Formula I and Y denoted in Formula II, respectively.

4. The coupler of claim 2, wherein said coupler is represented by the following Formula IV; Formula IV



10 wherein  $R_1$ ,  $R_2$ , and  $R_3$  are each synonymous with  $R$  denoted in Formula I, and  $X$  and  $Y$  are synonymous with  $X$  denoted in Formula I and  $Y$  denoted in Formula II, respectively.

5. The coupler of claim 4, wherein said coupler is represented by the following coupler V:  
Formula V



20 wherein  $R_1$ ,  $R_2$ , and  $R_3$  are each synonymous with  $R$  denoted in Formula I; and  $X$  is synonymous with  $X$  denoted in Formula I.

25 6. The coupler of claims 1, 2, 3, 4 or 5, wherein said coupler is added to a silver halide emulsion layer in an amount of from  $1 \times 10^{-3}$  mol to 1 mol per mol of silver halide.

30 7. The coupler of claim 6, wherein said coupler is added to a silver halide emulsion layer in an amount of from  $1 \times 10^{-2}$  mol to  $8 \times 10^{-1}$  mol per mol of silver halide.

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